BROMINE

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Bromine is one of two elements that are liquid at normal temperatures. Bromine is found principally in seawater, salt lakes, and underground brines associated with oil. In 2003, the quantity of bromine sold or used in the United States was 216 million kilograms (Mkg) valued at $155 million (table 1). The average value of bromine sold or used was $0.72 per kilogram (table 1). Primary uses of bromine compounds were in flame retardants, drilling fluids, brominated pesticides (mostly methyl bromide), and water-treatment chemicals. World production of bromine, in descending order and percentage of total for 2003 was estimated to be as follows: the United States, 39%; Israel, 38%; China, 8%; the United Kingdom, 6%; and other countries, 9% (table 5). Because of depleting reserves, distribution and economics, environmental constraints, and the emergence of Israel as the world's second largest producer, the U.S. portion of world production has decreased steadily since 1973 when the United States produced 71% of the world's supply.

Legislation and Government Programs

The cost of security and the price of natural gas had a depressing effect on the U.S. chemical industry, including bromine. The largest end use for bromine is in flame retardants that go into plastic products. Prices for petroleum and natural gas during 2003 began to increase, and industry called for a domestic energy policy. Natural gas used for electrical energy generation and heating competed with chemicals for plastics as natural gas prices trended above historical levels in 4 out of the past 5 years.

The chemical industry was reacting to a decrease in energy supply and an increase in energy demand. Eleven large chemical industries wrote a joint letter to the executive and legislative branches of the Federal Government requesting a concerted national effort to promote greater energy efficiency, accelerated efforts to reduce the use of natural gas in the electricity sector, aggressive Federal agency action to expedite drilling permits, and the immediate approval of the U.S. Department of Interior's (DOI) Minerals Management Service's rulemaking on royalty relief for deep gas drilling in existing wells in shallow waters (Chang, 2004, p. 2).

The DOI's Bureau of Land Management (BLM) released a final decision regarding oil and gas development on Montana and Wyoming public lands after more than 2 years of consideration in cooperation with the U.S. Department of Agriculture's (USDA) Forest Service and the U.S. Environmental Protection Agency (EPA). As many as 66,000 new coalbed methane wells could be drilled in the region by 2011. BLM officials no longer have concerns about compliance with clean air and clean water rules, for example, in Wyoming, BLM requested producers to consider a water management plan that would maximize deeper aquifer recharge in the Powder River basin rather than discharging downstream (Lorenzetti, 2003, p. 26).

As a result of the Maritime Transportation Security Act of 2002, the U.S. Coast Guard (USCG) can bypass the Administrative Procedures Act and issue regulations as "final" without a proposal stage. During 2003, the USCG implemented a review of complex regulations intended to make U.S. ports safe from terrorist attack. The USCG stated that the regulations will affect more than 10,000 ships per year entering some 350 ports. Bromine, a hazardous substance, is imported from Europe and the Middle East. The USCG held port security meetings around the country that were attended by 2,100 people and generated 900 pages of comments. The USCG regulations require facility owners or operators to designate a security officer, to provide plant security training, to conduct a facility security assessment, and to develop and implement a facility security plan by July 1, 2004 (Johnson, 2003).

Methyl bromide was listed as a class I ozone-depleting substance in the 1990 Clean Air Act (CAA) and was scheduled to be phased out of use in the United States by January 1, 2001. The U.S. Congress extended the deadline until January 1, 2005, to coincide with the deadline for phaseout of methyl bromide for developed countries under the Montreal Protocol on Substances That Deplete the Ozone Layer. Under the CAA Amendments of 1990 (CAAA) (Public Law 101-549), U.S. production and imports of bromine must be reduced from 1991 levels as follows: 25% by 1999; 50% by 2001; 70% by 2003; and a full ban by 2005. Domestically, methyl bromide had proven to be a difficult pesticide to replace because of its low cost and usefulness against a large variety of agricultural pests. The CAAA allowed for the exemption of critical uses of methyl bromide that had not yet been defined. The EPA evaluated these applications based on technical and economic criteria and developed with other agencies a nomination package that was submitted to the Secretariat of the Montreal Protocol in February 2003 (U.S. Environmental Protection Agency, 2003§[1]). The dominant use of methyl bromide was in soil treatments. It also was used in chemicals for termite treatment. Three producers—Albemarle Corp., Great Lakes Chemical Corp., and Israel's Dead Sea Bromine Co. Ltd. (DSB)—were the major manufacturers, accounting for 75% of global production. Autofina S.A. (Paris) was the only manufacturer of methyl bromide in Western Europe. Under the Montreal Protocol, developing countries had until 2015 to phase out methyl bromide production.

Countries may request exemptions from phaseout requirements for uses where there are no feasible technical or economical alternatives. Testimony as part of congressional hearings on methyl bromide pointed out that Chile, China, and Mexico, will be able to use the chemical until 2015 and that any environmental benefits from reduced use in the United States would be negated by such

[1]References that include a section mark (§) are found in the Internet References Cited section.

countries as China, which was estimated to have increased its use tenfold (Chemical Market Reporter, 2003d, p. 13). After a joint EPA-USDA technical review, the United States made a formal request to the Ozone Secretariat of the United Nations to allow use of methyl bromide after the January 1, 2005, phaseout deadline. The exemption would allow methyl bromide consumption in 2005 at 39% of the total 1991 consumption level and in 2006 at 37% of the 1991 level. The exempted uses included commodity storage, food processing, and treatment of eggplants, forest seedlings, peppers, strawberries, sweet potatoes, and tomatoes. The Technology and Economic Assessment Panel of the United Nations, approved the request for exemption from the 2004 ban for such U.S. crops as eggplants, raspberries, strawberries, and tree seedlings as well as for certain agricultural uses in other countries, such as Australia and France (Chemical & Engineering News, 2003c, p. 29).

The EPA published the direct final rule in the *Federal Register* on July 25, 2003, to regulate the export, import, and production of substances that deplete the ozone layer under the CAA. The rule was effective on October 23, 2003, without further notice. The EPA published the rule without prior proposal because it was viewed as a noncontroversial amendment and anticipated no adverse comment owing to the fact that the U.S. Senate gave its advice and consent to ratify the Montreal Amendment on October 9, 2002, and the rule simply adopts the provisions contained in that amendment. Entities potentially regulated by this action are those associated with the import and export of methyl bromide.

Bromine was taxed under the Comprehensive Environmental Response, Compensation, and Liability Act (Superfund) that was established in 1980 and funded in part by special taxes on the chemical and petroleum industries and an environmental tax on corporations. The Superfund had gone through two reauthorizations before Congress allowed the Superfund taxes to expire at yearend 1995; legislative attempts to reinstate the fund had not passed by yearend 2003. The EPA continued to add about 500 sites per year to the National Priorities List of about 44,000 potentially polluted sites. Other financial problems that face Superfund cleanups are bankruptcies of responsible parties and budgetary constraints of State governments, which sometimes share cleanup costs (Chemical Market Reporter, 2003f, p. 3).

The U.S. Consumer Product Safety Commission (CPSC) was developing a flammability performance standard for upholstered furniture using brominated fire retardants (BFRs). Residential fires in which upholstered furniture was the first item ignited account for more fire deaths than any other category of consumer products. The CPSC staff assessed potential health risks associated with the use of eight selected fire retardant (FR) compounds that were either those most likely to be used or those posing the greatest potential health concern. CPSC continued to gather information on FR materials that may be used to meet a CPSC standard (Babich and Thomas, 2002§).

In August, California became the first State to ban two polybrominated diphenyl ethers (PBDE) after testing showed the chemical accumulated in humans; the ban will take effect in 2008. The campaign in California received a boost when the European Union (EU) banned the use of two of the three main PBDE compounds earlier in the year. In 1976, Directive 76/769/EEC was adopted to establish restrictions on the marketing and use of certain dangerous substances and preparations in the EU. The substances listed in the annex can be either restricted in some applications or banned from the EU market, depending on the conditions specified. This directive has been amended several times in order to extend its scope of application to other substances.

The 24th amendment of February 6, 2003, prohibits the use of the brominated flame retardants penta-BDE and octa-BDE in all applications for the EU market from August 15, 2004. Developed in the early 1970s, PBDEs are used as FR in products from air dryer casings, carpet padding, carpets, computer casings, draperies, insulation, mattresses, paints, and polyurethane foam. The chemicals were first discovered in the environment in Sweden in the early 1980s. PBDEs were manufactured by Great Lakes Chemical Corp., Indianapolis, IN; Albemarle Corp., Richmond, VA; and Dead Sea Bromine Group, a unit of Tel Aviv-based Israel Chemicals Ltd. About one-quarter of the 239,000 metric tons (t) of the PBDEs produced globally in 2001 were consumed in the United States. Of the three main PBDE compounds, the California ban affects two, which are used in furniture and some plastics. The third PBDE compound, which is used in plastic casings of computers and televisions, has not been shown conclusively to accumulate in humans. This compound, however, represents more than 95% of the PBDE used each year. Researchers are now studying how PBDE move out of products and into humans. Preliminary tests showed high concentrations indoors on window grime and household dust (Schmidt, 2004, p. 70, 72).

Great Lakes settled a class-action lawsuit filed against the company for price fixing certain bromine-based products. The company took a charge against earnings to account for the cost of the settlement, which included $4.1 million in cash and $2.6 million in vouchers for the future purchases of decabromodiphenyl oxide and tetrabromobisphenol-A to be distributed to members of the class. The settlement converted 10 Federal class-action lawsuits into one Federal suit in the District Court for the Southern District of Indiana. Five California class-action cases were still pending in 2003 (Walsh, 2003, p. 8).

Production

Domestic production data for bromine were developed by the U.S. Geological Survey from a voluntary canvass of U.S. operations. Of the operations to which a canvass form was sent, seven responded, representing 100% of total U.S. elemental bromine production (table 2).

Albemarle's bromine production came from plant sites in southern Arkansas. Albemarle launched Saytex RX 8500 BFR, which was billed as an alternative to penta-PBDE in polyurethane foam applications. During 2003, Albemarle sold BFRs for use in solid thermoplastics as follows: acrylonitrile butadiene styrene (ABS) applications of six BFRs that ranged from 59% to 83% bromine; high-impact polystyrene applications (HIPS) of 11 BFRs that ranged from 59% to 83% bromine; polyamide applications of six BFRs that ranged from 53% to 83% bromine; polycarbonate applications of nine BFRs that ranged from 53% to 83%; polyethylene

applications of five BFRs that ranged from 67% to 83% bromine; polypropylene applications of 10 BFRs that ranged from 64% to 83%; and thermoplastic polyester applications of seven BFRs that ranged from 67% to 83% bromine (Albemarle, 2004§).

Ethyl Corp. billed Albemarle for $3.7 million related to asbestos liability obligations. In a Securities and Exchange Commission filing, Ethyl claimed that Albemarle was responsible for certain current and future liability claims under an indemnification agreement between the parties dated February 1994 (Chemical Market Reporter, 2003e, p. 4).

Great Lakes continued production of bromine from brines at plants in Arkansas. The company also owned Associated Octel Co. Ltd. of the United Kingdom, which produced bromine from seawater. Great Lakes, the only domestic producer of penta-bromodiphenyl ether (BDPE) voluntarily agreed to phase out production of two controversial PBDE flame retardants, penta- and octa-BDPE, by yearend 2004. The phaseout followed a review of a penta-BDPE replacement, Firemaster 550, which is a halogenated aryl ester and phosphate blend. Tests found that Firemaster 550 did not persist in the environment or bioaccumulate and was not toxic. Firemaster 550 will be used in polyurethane foam applications, such as furniture cushions, where penta-BDPE had been used. Production of Firemaster 550 will be scaled up by Great Lakes by yearend 2004 (Tullo, 2003, p. 13).

Great Lakes announced cost reduction steps that included manufacturing consolidations and employment reductions of around 400 jobs or about 9% of its workforce. The restructuring was directed at the BFR operations within its polymer additives unit. The decision to downsize resulted from decreased demand from the electronics industry beginning in 2001, high material costs, and intense world competition (Chemical Market Reporter, 2003b, p. 2).

Calcium bromide, sodium bromide, and zinc bromide, collectively referred to as clear brine fluids (CBFs), were used in the oil- and gas-well-drilling industry for high-density, solids-free completion, packer, and workover fluids to reduce the likelihood of damage to the well bore and productive zone. TETRA Technologies, Inc. was one of the largest users of CBFs in the world. Calcium bromide and zinc bromide were purchased by TETRA from two domestic manufactures and one foreign manufacturer. TETRA also recycled calcium- and zinc-bromide CBFs repurchased from its oil and gas customers. Its West Memphis, AR, facility produced calcium bromide and zinc bromide from zinc-containing electroplating sludge and low-cost hydrobromic acid. TETRA began operation of an elemental-bromine, calcium-bromide, and sodium-bromide plant at Dow Chemical Co.'s Ludington, MI, facility in mid-1998, using purchased crude bromine from Dow's calcium-magnesium chemicals operation. The liquid sodium bromide was sold to the industrial water treatment markets. TETRA also owned a plant in Magnolia, AR that was designed to produce calcium bromide but was not operational in 2003 (TETRA Technologies, Inc., 2003§).

Consumption

The major use of bromine is as a fire retardant material that can be added to petroleum-based products to make them resist fire. On February 20, 2003, 99 people died in a fire in a Providence, RI, night club because the egg-crate-pattern material that was used as sound-proofing material was not treated with fire retardant. The padding used in upholstered furniture, including playpens and car seats, fuels fires that kill more than 1,000 people every year in the United States. Mattresses and bedding are the second leading cause of household fires. The two sources are blamed for 28,000 fires annually. Fires injure more than 3,400 people annually and cause nearly $1 billion dollars in property damage. The State of California enacted laws that require upholstered furniture to resist ignition by small open flames, such as matches and cigarettes. In the United States, non-Californians are seven times more likely to die from fires involving upholstered furniture than Californians. In 1993, the National Association of State Fire Marshals asked the Federal Trade Commission and the CPSC to set flammability standards for upholstered furniture (Lord, 2003).

Since 1995, the use of methyl bromide has decreased by more than 4.5 Mkg (10 million pounds), replacement fumigant metham sodium has increased by 1.9 Mkg (4.2 million pounds) (27%) and fumigant 1,3-dichloropropene has increased by 635,000 kg (1.4 million pounds) (35%). Pesticide use on crops in California surged by 14% during 2002. Consumption for all but 2 of the top 10 pesticides used in California increased as reported by individual counties. The use of chemicals classified as carcinogens increased by 15% but deceased in application area by 5%. An analysis by the California Department of Pesticide Regulation (DPR) showed higher acreage for several major crops that accounted for the increased pesticide use and noted that pesticide use varied from year to year, depending on acreage, crop pattern, economic conditions, pest, weather, and other factors. The DPR attributed the increase in pesticide use to less toxic pesticides, noting that use of more environmentally friendly compounds often requires heavier and more frequent applications (Chemical Market Reporter, 2003a, p. 26).

Arch Chemical Inc. acquired Avecia Ltd.'s biocide business for $215 million and captured a portion of the pool and spa market with 2003 sales of $52 million. Three principal EPA-registered technologies used in residential pools and spa sanitation are bromine, chlorine, and polyhexamethlenebiguanide (PHMB). Most swimming pools use a tablet that is 66% bromine and 27% chlorine (Lerner, 2004, p. 16).

Bromine is more unstable than chlorine in sunlight. As much as 7% of the free bromine in a pool can be depleted by the sun in 2 hours; however, when used with an effective oxidizer, small doses of bromine can be used as a disinfectant. Bromine is more effective than chlorine in hot water used in spas and hot tubs. Formulations typically have a low pH of 4.0 to 4.5, creating an acidic solution that can be adjusted by adding soda ash (DeKorne, 2003).

World Review

European Union.—The directive on waste electrical and electronic equipment (WEEE) aimed to increase the recycling and recovery of WEEE through mechanical recycling, feedstock recycling, and energy recovery. The directive will require recycling of

most electrical and electronic (E&E) equipment in Europe. Polymer producers of HIPS and ABS are likely to be the most affected because much of the E&E market is not accessible without the use of halogenated flame retardants (HFR), such as BFRs, because of the fire safety demands. Plastic compounds for E&E applications are typically polymer specific. To ban the use of HFRs could require prohibitively large investments in new processing equipment owing to individual polymer reliance on BFRs to meet the desired fire safety standards. In practice, in many EU countries, such as Denmark, separation of all flame retardant plastics will be required for WEEE. By December 31, 2006, the directive required the separation of at least 4 kg of WEEE per inhabitant per year. Out of this collected WEEE, manufacturers of information technology and telecommunication equipment must recover 75% by average weight of the appliance and 65% by average weight per appliance and of reused recycled component materials. European member states have to set up E&E waste collection facilities by August 13, 2005. Only two of the 75 BFRs used will be affected by the EU directive to restrict hazardous substances from E&E equipment. The directive gives producers a clear guarantee that no individual EU member state will be able to introduce separate bans or restrictions on any substance other than those specified in the directive (Bromine Science and Education Forum, 2003§). Concern by incinerator operators resulted in a study commissioned by the industry lobby group. The study concluded that the level of BFRs present in plastic appliance parts incinerated in municipal waste streams was below levels that could damage incinerators (Rademakers, Hesseling, and van de Wetering, 2002).

France.—Atofina Chemicals Inc. announced the successful recommissioning of its Port-de-Bouc plant in Bouches-du-Rhone, France, to manufacture brominated derivatives for use in pharmaceutical and other fine chemical intermediates. Atofina was formed in June 2000 following the merger of TotalFina and Elf Aquitaine. The recommissioning followed a 1-week shutdown in December 2002, when all units were brought up to standards of the International Organization for Standards. Recent investments include a brominated-acids/esters unit, a specialty brominated chemicals unit designed to manufacture pharmaceutical intermediates, and two ultrapure hydrobromic acid generators. The plant consists of the following: four multipurpose units specializing in brominated fine chemicals that produce alkyl bromides and dibromides, boron tribromide, phosphate tribromide, bromoacids and brominated esters; two ultrapure hydrobromide generators; a processing unit to make custom brominated compounds and intermediates; and the ability to recycle and recover brominated wastes (Atofina S.A., 2003). On December 1, Atofina was sold to Albemarle, Baton Rouge, LA (Bob Ash, Atofina Chemicals Inc., written commun., November 21, 2003). Included in the sale was the site near Marseille, France; the goodwill; the intellectual property; and the technology of the business that had sales in 2002 of about $30 million (Chemical & Engineering News, 2003a, p. 16).

Mines de Potasse d'Alsace S.A. (MDPA), produced bromine as a byproduct of potash production. The potash extraction program ceased in April 2003. The MDPA and Entreprise Minière et Chimique (EMC) were converting the buildings to private housing. Three core activities were planned to be completed by December 2004 as follows: financing MDPA post-mining operations in Alsace and supporting the redevelopment of the potassium basin; ownership through a holding company of participations of minority interest in chemicals, environmental services, and animal feed production; and supporting the expansion of international operations in Africa and Vietnam in the agricultural supplies and animal feed markets (Entreprise Minière et Chimique, 2004§).

Israel.—The Dead Sea Bromine Group (DSBG) announced price increases for its major flame retardant products that included the following BFRs: decabromodiphenyl oxide (DDPO) used in ABS, engineered plastics, HIPS, polyolefins, and textiles; tetrabromobisphenol-A used in ABS, epoxies, FR intermediates, phenolics, and polycarbonates (PC); tribromphenol used as an FR intermediate and for wood preservative applications; and brominated epoxy oligomers used in ABS, HIPS, PC/ABS alloys, nylon 6, nylon 66, polybutylene terephthalate, and polyethylene terephthalate. DSBG is the world's leading producer of elemental bromine and a leader in the development and supply of bromine compounds (Dead Sea Bromine Group, 2003). DSBG consists of four divisions that include industrial chemicals, flame retardants, soil treatment, and biocides. Manufacturing facilities are located in China, Israel, the Netherlands, and the United States. DSBG is a member of Israel Chemical Ltd. (ICL), which includes Dead Sea Works, which controls potash and salt, and Rotem, which controls fertilizers. ICL's shareholders include Israel Corp (53.23%), Potash Corp. of Saskatchewan (PCS) (9.03%), Bank Leumi asset management funds (6.4%), and the general public (31.32%) (Harben, 2003, p. 18-20).

Japan.—DSBG signed an agreement with Manac of Hiroshima to produce and market BFRs for engineering plastics that use Manac technology. DSBG received the rights to produce and market the flame retardant worldwide, and it will pay Manac royalties under the agreement.

Jordan.—The King, accompanied by the Industry and Trade Minister and U.S. Trade Representative, officially inaugurated Jordan Bromine Co. Ltd. (JBC) on June 23. The $123 million venture between Arab Potash Company (APC) and a U.S. subsidiary of Albemarle, Albemarle Holdings, will use brines from the Dead Sea to produce 50,000 t of bromine, 35,000 t of calcium bromide, and 50,000 t of tetrabromobisphenol for the Asian and European markets. By January 2005, Jordan planned to construct and have operational a 25,000-metric-ton-per-year (t/yr) membrane chlorine plant to support the growing demand for bromine. The second stage of the project will include a plant for chlorine and potassium hydroxide and a flake plan (Chemical Market Reporter, 2003c, p. 2). About 80 Jordanians are currently employed at the bromine production plant (Dajani, 2003§). On October 16, PCS purchased a 26% stake in APC that was offered for sale by the Jordan Investment Co. (JIC) for $173 million. The shares in APC are as follows: JIC (26.9%), PCS (26%), Arab Mining Co. (21%), and other Arab governments, banks, and individual investors (26.1%) (Green Market, 2003, p. 1-2).

Tajikistan.—In the southwest of the country, there are accumulations of underground mineralized water with concentrations of boron, bromine, iodine, lithium, and strontium. The Tut-Bulak deposit is 3.5 kilometers (km) east of Yavan and 13 km from the Yavansk Chemical Combine with reported values of 168 parts-per-million bromine. Technical evaluation of one cubic meter of the brines reported the possibility of 194 t of iron bromide (Engineering News, 2004, p. 65).

Turkmenistan.—The Ministry of Energy and Electricity announced investment opportunities in the following five iodine and bromine plants: the Goturdepe plant near Cheleken (1,300 t bromine), the Achak plant near Gasachakt (2,000 t bromine), and the Boyadag (2,500 t bromine), Gograndag (5,000 t bromine) and Nebitdag (3,000 t bromine) plants near Nebitdag. Also announced was the construction of a calcium bromide production facility at the Cheleken plant with a capacity of 1,000 t/yr (Turkmenistan Ministry of Energy, 1997§).

Current Research and Technology

Activated carbon is used to remove organic compounds from water through a process known as adsorption. Various researchers have studied the use of activated carbon and have concluded that it is cost-effective for the reduction of bromate. However, not all carbon removal processes are alike, especially when chemical reactions control the process. Bromate is a disinfection byproduct formed by the reaction of ozone and naturally occurring bromine in drinking water. There is some evidence that commercially available sodium hypochlorite solutions may contain bromate as a contaminant. Bromate is a highly toxic substance that can cause irreversible renal failure, deafness, and death in humans and has been linked to renal tumors in rats. The important precursor to bromate formation in drinking water is bromide. Natural sources of bromine in groundwater are salt water intrusion and bromide dissolution from sedimentary rocks. In addition to bromate, aqueous bromine can form various types of brominated disinfection byproducts, such as bromoform and brominated haloacetic acids. A test study that used a 30-minute contact time and catalytically enhanced 8 x 30-mesh carbon showed bromate could be successfully reduced from an average of 100-parts-per-billion (ppb) to an average of less than 5 ppb (Thompson and Megonnel, 2003).

Mixed salt brines, such as those that contain bromine, have a given density and true crystallization temperature (TCP), although the references do not provide compositions for these pressurized crystallization temperatures (PCT). A method used to calculate brine crystallization temperature at elevated pressure was within 3° F (1.67° C) of the measured value and can aid in processing deepwater brines to prevent crystallization during processing. For mixed salt systems, however, a method used to determine the density, TCP, and weight percent of water for the brine, was to evaporate enough water to increase the brine's density, measure the brine's TCP and density, add water while measuring the TCP density until the initial density was obtained, and plot TCP versus density (Vollmer, 2003).

PBDE, which is used to make furniture, foam, and electronics fire resistant, was found in high concentrations in the breast milk of women in the United States. Breast milk was tested because it is the least invasive way to test fat where PBDE is stored. Although the study was inconclusive in determining how the PBDE entered breast milk, experts advise new mothers to continue breast feeding. Exposure through breast milk may be minor compared with the impact in utero. The health effects of exposure to PBDE in humans are unknown. Studies in rats and mice have found that low levels may cause cognitive and behavioral changes during development. Breast milk has immunological qualities that help protect babies and may help babies fight environmental contaminants (Weise, 2003).

A group of researchers at Purdue University tested the solar stability of the decabrominated (DBDE) form of PBDE and found that it was found in increasing amounts in the environment. In two tests, the DBDE decayed into molecules that contained less bromine than the original compound. In 1999, DBDE accounted for about 80% of the PBDE manufactured worldwide (Chemical & Engineering News, 2003b, p. 31).

Conducting polymers were first created in the 1970s and were used in small-scale commercial applications, such as antistatic coating on photographic film and light emitting diodes in a display of maintenance information on an electric razor. Conducting polymers are produced by adding small amounts of bromine or iodine gas to plastic to remove some electrons. Called doping, this process allows the remaining electrons to move rapidly up and down the polymer's chains. Studies are being conducted on paper-thin televisions and sensors for chemical-weapons detectors. Molecular disorder limits the polymer's conductivity and performance in electronic devices. Researchers are trying to determine how to make plastic more orderly on the molecular level. The original polyacetylene polymer decomposed quickly in air. A more stable class of conducting polymer called polythiophenes was formulated in 2000 using bromine. Electronically conducting materials based on conjugated polymers have been applied in such diverse items as biomaterials, corrosion protection agents, light-emitting diodes, sensors, and polymer actuators (Gorman, 2003, p. 312).

A scientist looking for the blue dye used for the blue string on the corners of the Israelite prayer shawl referenced in the Bible as "chilazon" gathered Murex trunculus snails for research. The Arab word for mollusk is chilzun. The clear yellow substance extracted from the mollusk proceeded through a complex enzymatic reaction before it stabilizes at an intense deep purple upon exposure to air. Further research revealed that when the dibromoindigo dye was exposed to the sun for a few minutes, the bromine broke from the molecule leaving behind only indigo, the brilliant biblical blue (Greenspan, 2003, p. 96).

Outlook

Fire Retardants.—Bromine is used as an FR in plastics and also acts in synergy with many other materials to increase the overall effectiveness of the FR. FRs accounted for between 40% and 50% of domestic demand for bromine. Although usage fluctuates along with overall cycles in the economy, demand was expected to grow by 4% per year, assuming sustained economic growth (Chemical Products Synopsis, 2003, p. 1-2). Environmental and health concerns about two PBDP compounds resulted in their use being banned in some markets and voluntarily withdrawn in other markets, resulting in a decreased demand between 2001 and 2003. Recycling efforts in Europe for BFR plastics in electrical usage, which is easier to recycle than some other flame retardant compounds, may

increase the demand for these brominated products because they are thought to be more environmentally friendly, especially by countries concerned about recycling, such as Japan. Growth was expected to increase overall in BFRs if the fire safety standards for upholstered furniture and roofing materials and if higher flammability standards were voluntarily adopted in televisions produced in Europe (Markarian, 2003.

Petroleum.—Demand for bromine as a gasoline additive has declined each year since the EPA issued regulations in the 1970s to reduce and eliminate lead in automotive gasoline. In 1979, the amount of bromine sold for this application reached a peak of 225 Mkg. The rapid decline to 141 Mkg in 1986 was a direct result of the limits on lead in leaded automotive gasoline. The CAA requires mobile sources, such as cars and trucks, to use the most effective technology possible to control emissions. Newer prototypes of the fuel cell that burn gasoline can double the mileage and decrease emissions by using unleaded gasoline or other nonbrominated fuels. Use of calcium-, sodium-, and zinc-bromides in oil-well-completion fluids has benefited in recent years from the rebound in world oil prices and the increased demand for petroleum products. Natural gas used to produce electricity competed with chemicals for plastics.

In 2003, the oil services sector posted a strong performance. The Baker Hughes rig count from Baker Hughes Inc. showed an increase of 77% compared with that of 2002. The Smith rig count of Smith International Inc. showed about a 4% increase in drilling of wells deeper than 3,050 meters (10,000 feet). Oilfield chemicals used in drilling, completion and workover, and production operations remained significantly more profitable internationally than in the United States. Use of calcium, sodium, and zinc bromides in oil-well-completion fluids has benefited in recent years from the rebound in world oil prices.

Sanitary Preparations.—The growth potential remains high for bromine-based biocides for use in industrial cooling systems because of environmental restrictions on chlorine and new alkaline-base chemical treatment programs. The most common bromine compounds used in cooling water are 1-bromo-3-chloro-5,5-dimethylhydantoin and mixtures of sodium bromide with sodium hypochlorous acid. Bromine was used in indoor swimming pools, hot tubs, and whirlpools. The sanitary preparation field is an area where bromine was found to be safer than its substitutes because bromine has a higher biocidal activity level for the same volume of product. The use of bromine compounds was increasing in the spa and hot tub sector and was being used with chlorine in swimming pools as a kinder and gentler disinfectant.

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TABLE 1

SALIENT BROMINE AND BROMINE COMPOUNDS STATISTICS[1]

(Thousand kilograms and thousand dollars)

	HTS[2] number	1999	2000	2001	2002	2003
United States:						
Bromine sold or used:[3]						
Quantity		239,000	228,000	212,000	222,000	216,000
Value		213,000	206,000	159,000	166,000	155,000
Exports:[4, 5]						
Elemental bromine:	2801.30.2000					
Quantity		2,110	1,870	3,710	6,070	2,280
Value		2,430	2,560	3,600	4,680	3,090
Bromine compounds:[6]	(7)					
Gross weight		9,520	9,210	7,990	8,000	7,160
Contained bromine		8,020	7,740	6,740	6,750	6,040
Value		16,000	26,200	14,900	13,600	11,800
Imports:[4, 8]						
Elemental bromine:	2801.30.2000					
Quantity		1,970	5,470	5,610	2,020	1,920
Value		2,110	3,730	4,240	1,530	1,450
Bromine compounds:						
Ammonium bromide:	2827.59.2500					
Gross weight		1,510 [9]	48,100	59,700	16,900	46,600
Contained bromine		1,240	3,930	4,870	1,380	3,800
Value		1,940	22,000	29,200	8,850	21,100
Calcium bromide:	2827.59.2500					
Gross weight[9]		--	7,860	5,880	164	9
Contained bromine		--	6,280	4,700	131	7
Value		--	4,780 [e]	3,580 [e]	100 [e]	4 [e]
Potassium bromate:	2829.90.0500					
Gross weight		373	245	124	126 [9]	131 [9]
Contained bromine		178	117	59	36	63
Value		1,470	1,100	450	457 [e]	475 [e]
Potassium bromide:[10]	2827.51.0000					
Gross weight		1,170	871 [9]	433 [9]	171 [9]	497
Contained bromine		786	585	291	115	334
Value		2,830 [e]	2,130	1,060 [e]	417 [e]	1,210 [e]
Sodium bromate:	2829.90.2500					
Gross weight		1,050	1,160	1,020	1,020	967
Contained bromine		554	615	538	539	512
Value		2,430 [e]	2,750	2,190	2,020	2,010
Sodium bromide:[10]	2827.51.0000					
Gross weight[9]		4,640	3,130	NA	2,980 [9]	3,670 [9]
Contained bromine		3,600	2,430	NA	2,320	2,940
Value		5,540 [e]	4,820 [e]	NA	4,600 [e]	5,660 [e]
Other compounds:						
Gross weight		7,400	7,760	5,950	4,920	3,280
Contained bromine		785	582	141	176	246
Value		17,000	15,500	5,360	6,090	19,000
World, production[e]		547,000	542,000	523,000	540,000 [r]	548,000

[e]Estimated. [r]Revised. NA Not available. -- Zero.

[1]Data are rounded to no more than three significant digits.

[2]Harmonized Tariff Schedule of the United States (HTS).

[3]Elemental bromine sold as such to nonproducers, including exports, or used by primary U.S. producers in preparing bromine compounds.

[4]Source: U.S. Census Bureau.

[5]Export values are free alongside ship.

[6]Source: U.S. Census Bureau. Includes methyl bromine and ethylene dibromide.

[7]Data for these compounds are derived from HTS number 2903.30.0500 (2001 and 2002), 2903.30.1500 (1999), and 2903.30.1520 (2000, 2002, and 2003) information.

[8]Import values are cost, insurance, and freight.

[9]Source: The Journal of Commerce Port Import/Export Reporting Service.

[10]"Potassium bromide" and "Sodium bromides" import data are usually reported by a mutual HTS number, 2827.51.0000.

TABLE 2
ELEMENTAL-BROMINE-PRODUCING PLANTS IN THE UNITED STATES IN 2003

State and company	County	Plant	Production source	Capacity[1] (million kilograms)
Arkansas:				
Albemarle Corp.	Columbia	Magnolia (a)	Well brines	
Do.	do.	Magnolia (b)	do.	123 [2]
Great Lakes Chemical Corp.	Union	El Dorado (a)	do.	
Do.	do.	El Dorado (b)	do.	71 [2]
Do.	do.	Maryville	do.	36
Do.	do.	Newell	do.	23
Michigan, The Dow Chemical Co.	Mason	Ludington[3]	do.	9
Total				262

[1]Actual production capacity is limited by brine availability.
[2]This represents the cumulative capacity of the two identified plant sites.
[3]Bromine produced at this plant is reprocessed in Arkansas.

TABLE 3

U.S. IMPORTS OF OTHER BROMINE COMPOUNDS[1, 2]

Compound	HTS[3] number	2002 Gross weight (kilograms)	2002 Value[4] (thousands)	2003 Gross weight (kilograms)	2003 Value[4] (thousands)	Principal sources, 2003
Hydrobromic acid	2811.19.3000	360	$278	215	$255	Israel, 99%.
Ethylene dibromide	2903.30.0500	(5)	10	88	100	United Kingdom, 100%.
Methyl bromide	2903.30.1520	430	1,440	356	1,220	Israel, 92%, China, 8%.
Dibromoneopentyl glycol	2905.50.3000	1,010	3,350	1,140	3,800	Israel, 98%.
Tetrabromobisphenol A	2908.10.2500	832	1,210	452	1,020	Israel, 100%.
Decabromodiphenyl oxide and octabromodiphenyl oxide	2909.30.0700	2,290	4,320	3,300 [6]	6,210 [e]	Israel, 100%.
Total		4,920	10,600	5,550	12,600	

[e]Estimated.

[1]These data detail the information included in table 1 under "Imports, bromium compounds, other compounds."

[2]Data are rounded to no more than three significant digits; may not add to totals shown.

[3]Harmonized Tariff Schedule of the United States.

[4]Declared cost, insurance, and freight valuation.

[5]Less than 1/2 unit.

[6]Source: The Journal of Commerce Port Import/Export Reporting Service.

Source: U.S. Census Bureau.

TABLE 4

WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES AS OF DECEMBER 31, 2003[1]

Country and company or plant	Location	Capacity (thousand kilograms)	Source
Azerbaijan, Neftechala Bromine Plant	Baku	4,000	Underground brines.
China, Laizhou Bromine Works	Shandong	30,000	Do.
France:			
Albemarle	Port-de-Bouc	12,000	Seawater.
Mines de Potasse d'Alsace S.A.	Mulhouse		Closed.
India:			
Hindustan Salts Ltd.	Jaipur		Seawater bitterns from salt production.
Mettur Chemicals Ltd.	Mettur Dam	1,500	
Tata Chemicals Ltd.	Mithapur		
Israel, Dead Sea Bromine Co. Ltd.	Sdom	190,000	Bitterns of potash production from surface brines.
Italy, Societa Azionaria Industrial Bromo Italiana	Margherita di Savoia	900	Seawater bitterns from salt production.
Japan, Toyo Soda Manufacturing Co. Ltd.	Tokuyama	20,000	Seawater.
Spain, Derivados del Etilo S.A.	Villaricos	900	Do.
Turkmenistan:			
Nebitag Iodine Plant	Vyshka	3,200	Underground mines.
Cheicken Chemical Plant	Balkan	6,400	Do.
Ukraine, Perekopskry Bromine Plant	Krasnoperckopsk	3,000	Do.
United Kingdom, Associated Octel Co. Ltd.	Amlwch	30,000	Seawater.

[1]Excludes U.S. production capacity, which is detailed in table 2.

TABLE 5

BROMINE: ESTIMATED WORLD REFINERY PRODUCTION, BY COUNTRY[1, 2]

(Thousand kilograms)

Country[3]	1999	2000	2001	2002	2003
Azerbaijan	2,000	2,000	2,000	2,000	2,000
China	42,000	42,000	40,000	42,000	42,000
France	1,950	2,000	2,000	2,000	2,000
Germany	500	500	500	500	500
India	1,500	1,500	1,500	1,500	1,500
Israel	181,000 [4]	210,000 [4]	206,000	206,000	206,000
Italy	300	300	300	300	300
Japan	20,000	20,000	20,000	20,000	20,000
Jordan	-- [4]	-- [4]	-- [4]	5,000 [r, 4]	20,000
Spain	100	100	100	100	100
Turkmenistan	150	150	150	150	150
Ukraine	3,000	3,000	3,000	3,000	3,000
United Kingdom	55,000 [4]	32,000 [4]	35,000 [4]	35,000	35,000
United States[5]	239,000 [4]	228,000 [4]	212,000 [4]	222,000 [4]	216,000 [4]
Total	547,000	542,000	523,000	540,000 [r]	548,000

[r]Revised. -- Zero.

[1]World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[2]Table includes data available through April 16, 2004.

[3]In addition to the countries listed, several other nations, including Iran, produced bromine, but output data were not reported; available general information is inadequate to formulate reliable estimates of output levels.

[4]Reported figure.

[5]Sold or used by producers.